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Reaction of 1-Germatranol Hydrate with Carboxylic Acids

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Abstract—Reaction of 1-germatranol hydrate with carboxylic acids RCOOH (R = $ClCH_2$, PhCH=CH, Ph, 2-FC_6H_4, 3-BrC_6H_4, 3-HOC_6H_4, 3-$EtOC_6H_4$) in protic (CH_3OH, *iso*-$C_5H_{11}OH$) and aprotic polar solvent (CH_3CN) is studied. 1-Acyloxygermatranes $RC(O)OGe(OCH_2CH_2)_3N$ are formed in yields from 11 to ~100 % depending on the nature of the acid, solvent, duration of the process and the method of its completion. The reaction is the most effective in acetonitrile. Its topochemical completion (heating of the reaction residue in a vacuum) increases the yield of 1-acyloxygermatranes.

Keywords: hydrate of 1-germatranol, esterification, carboxylic acids, topochemical reaction

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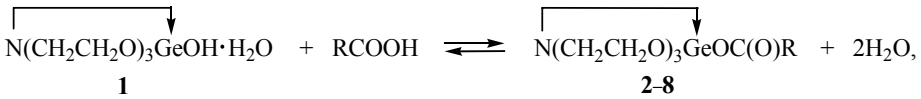
Intracomplex tricyclic silicon and germanium ethers of triethanolamine, silatranes and germatranes, as a rule, possess similar biological activity [1, 2]. The adducts of germatranes, including 1-germatranol, with compounds containing carboxy group and showing high physiological activity were patented [3–7].

The first 1-acyloxygermatrane, 1-acetoxygermatrane $CH_3C(O)OGe(OCH_2CH_2)_3N$, was prepared in 91% yield by the reaction of 1-methoxygermatrane with 98% acetic acid and its anhydride in *o*-dichlorobenzene at 100°C [8,9]. Later on, from 1-methoxygermatrane and the corresponding carboxylic acids 1-dichloro-acetoxy- and 1-diphenylacetoxygermatrane were obtained [10]. A series of 1-acyloxygermatranes was synthesized by the reaction of 1-chlorogermatrane with potassium salts of carboxylic acids [11]. By successive reaction of germanium dioxide with triethanolamine and carboxylic acids in *o*-xylene and isopentanol we have recently prepared 1-acyloxygermatranes with the following substituents in the acyl group RC(O): R = CH_3, 2-$MeC_6H_4CH_2OCH_2$, C_6H_5, 2-HOC_6H_4 [12].

In the present work the reaction of 1-germatranol hydrate $N(CH_2CH_2O)_3GeOH\cdot H_2O$ (**1**) with carboxylic acids in polar solvents methanol and acetonitrile is studied in comparison with the reaction in isopentanol and xylene.



$$N(CH_2CH_2O)_3GeOH\cdot H_2O\ (\mathbf{1}) + RCOOH \rightleftharpoons N(CH_2CH_2O)_3GeOC(O)R\ (\mathbf{2\text{–}8}) + 2H_2O, \quad (1)$$

R = $ClCH_2$ (**2**), C_6H_5CH=CH (**3**), C_6H_5 (**4**), 2-FC_6H_4 (**5**), 3-BrC_6H_4 (**6**), 3-HOC_6H_4 (**7**), 3-$C_2H_5OC_6H_4$ (**8**).

The yields increased with the duration of the reaction (Table 1). In the reaction of **1** with cinnamic acid, apart from product **3**, 1-isoamyloxygermatrane **9** is formed; its content in the reaction mixture slightly increases (from 5.1 to 5.5%) on growth the time of heating in isoamyl alcohol from 6 to 15 h.

Since the reaction of 1-germatranol with carboxylic acids is reversible, azeotropic distillation of water presumably would give better results as compared to the process without removal of water. However, the highest yields of 1-acyloxygermatranes were obtained by carrying out the reaction in acetonitrile, especially

Table 1. Yields of 1-acyloxygermatranes RCOOGe(OCH$_2$CH$_2$)$_3$N in reaction of 1-germatranol hydrate **1** with carboxylic acids

Comp. no.	R	Reaction conditions	Yield,[a] %
2	$ClCH_2$	CH_3CN, 80°C, 6 h	90.8[b]
		CH_3CN, 80°C, 12 h	92.4[b]
3	*trans*-C_6H_5CH=CH	*iso*-$C_5H_{11}OH$, 130°C, 6 h	59.3
		iso-$C_5H_{11}OH$, 130°C, 15 h	72.9
		CH_3OH, 64°C, 3 h	11.3
		CH_3OH, 64°C, 3 h	57.0[b]
		CH_3OH–H_2O (9 : 1 v/v), 64°C, 3 h	6.9
		CH_3OH–H_2O (9 : 1 v/v), 64°C, 3 h	29.5[b]
		CH_3CN, 80°C, 6 h	90.9[b]
4	C_6H_5	*iso*-$C_5H_{11}OH$, 130°C, 1 h	82.0 [12]
		CH_3OH, 64°C, 7 h	31.6
		CH_3CN, 80°C, 1 h	93.5[b]
5	2-FC_6H_4	CH_3CN, 80°C, 2 h	18.9
		CH_3CN, 80°C, 4 h	53.2
		CH_3CN, 80°C, 6 h	99.6[b]
6	3-BrC_6H_4	CH_3CN, 80°C, 6 h	96.0[b]
7	3-HOC_6H_4	*o*-$C_6H_4(CH_3)_2$, 143°C, 7 h	81.2
		o-$C_6H_4(CH_3)_2$, 143°C, 10 h	98.3
		iso-$C_5H_{11}OH$, 130°C, 3 h	59.8
		iso-$C_5H_{11}OH$, 130°C, 6 h	88.9
		iso-$C_5H_{11}OH$, 130°C, 12 h	96.9
8	3-$C_2H_5OC_6H_4$	*o*-$C_6H_4(CH_3)_2$, 143°C, 17 h	44.9
		iso-$C_5H_{11}OH$, 130°C, 3 h	47.0
		iso-$C_5H_{11}OH$, 130°C, 12 h	79.3
		CH_3CN, 80°C, 7 h	89.0
		CH_3CN, 80°C, 7 h	93.2[b]

[a] Calculated from integral intensities of the OCH_2 and NCH_2 group protons in ^{1}H NMR spectra of the reaction mixtures. [b] Dried reaction mixture kept for 1 h at 50°C in a vacuum of 2 mmHg.

when the dry residue after the reaction was heated in a vacuum. The reaction between 1-germatranol hydrate **1** and cinnamic acid in boiling acetonitrile for 6 h with subsequent exposure of the dry reaction residue for 1 h at 50°C to the vacuum of 2 mmHg gives product **3** in 90.9% yield (Table 1). The reaction of **1** with 3-ethoxybenzoic acid in acetonitrile after 7 h of reflux gives the yield of 89.0%, whereas after exposure of the dry reaction residue to a vacuum at 50°C the yield reaches 93.2%.

Carrying out the reaction with heating of the reaction residue in a vacuum turned out to be effective also for other acids (Table 1). Under these conditions, the yields in all cases exceed 90%, and with 2-fluorobenzoic acid 1-(2'-fluorobenzoyloxy)germatrane **5** is formed in quantitative yield and does not require additional purification.

The reaction of 1-germatranol with cinnamic acid in protic solvent methanol at reflux in the course of 3 h leads to the formation of only 11.3% of 1-(benzylideneacetato)germatrane **3**. Along with this, 1-methoxygermatrane **10** (7.6%) and bis(germatran-1-yl)oxane **11** (4.2%) are formed [schemes (2a)–(2d)].

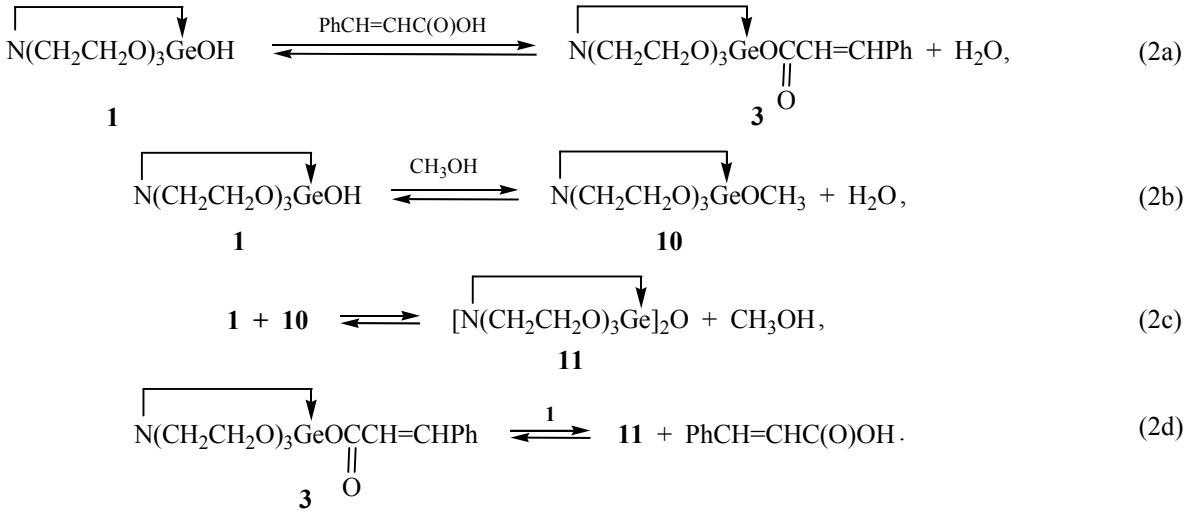
Earlier it was established that direct reaction of **1** and **11** with methanol follows equations (2b) and (2c) [13]. It is hardly probable that under these conditions bis(germatran-1-yl)oxane **11** is formed also due to elimination of water molecule from two molecules of **1**. The latter reaction proceeds only on heating **1** to 220°C in a vacuum [14].

In the system methanol–water (9 : 1 v/v) the yield of product **3** is twice as low as in nonaqueous methanol. The content of 1-methoxygermatrane **10** and

Table 2. Melting points and elemental analysis data of 1-acyloxygermatranes $RC(O)OGe(OCH_2CH_2)_3N$

Comp. no.	R	mp, °C (acetonitrile)	Found, %				Formula	Calculated, %			
			C	H	Ge	N		C	H	Ge	N
2	$ClCH_2$	178–180	30.50	4.33	23.05	4.81	$C_8H_{14}ClGeNO_5$	30.77	4.52	23.25	4.49
3	*trans*-C_6H_5CH=CH	189–190	48.56	4.97	19.42	4.04	$C_{15}H_{19}GeNO_5$	49.23	5.23	19.84	3.83
5	2-FC_6H_4	225–227	43.74	4.11	19.84	4.04	$C_{13}H_{16}FGeNO_5$	43.63	4.51	20.29	3.91
6	3-BrC_6H_4	179–181	37.12	3.60	16.89	3.49	$C_{13}H_{16}BrGeNO_5$	37.28	3.85	17.34	3.34
7	3-HOC_6H_4	222–223[a]	44.27	4.60	19.92	3.88	$C_{13}H_{17}GeNO_6$	43.87	4.81	20.40	3.94
8	3-$C_2H_5OC_6H_4$	127–129[b]	–	–	–	–	$C_{15}H_{21}GeNO_6$	–	–	–	–

[a] From isopentanol. [b] From chloroform.



bis(germatran-1-yl)oxane **11** (2.0%) in the reaction mixture is also notably decreased. Probably the presence of water in methanol shifts the equilibrium of esterification of **1** to the left [schemes (2a), (2b)]. Note that unlike their germatrane analogs, 1-acyloxysilatranes are much less hydrolytically stable than 1-alkoxysilatranes [15].

Keeping the solid reaction mass obtained from the reaction of 1-germatranol with cinnamic acid in aqueous methanol to constant mass in a vacuum of 2 mmHg at 40–50°C increases the yield of **3** more than four times (Table 1), apparently due to elimination of water.

1-Acyloxygermatranes **2**–**8** are soluble in acetonitrile and lower alcohols, insoluble in diethyl ether, alkanes. Their structure was proved by elemental analysis (Table 2), ^1H, ^{13}C NMR, and IR spectra (Table 3).

In the IR spectra of compounds **2**–**8** the absorption bands ν_{Ge-O-C}, ν_{C-O-C} (1000–1010, 1020–1060, 1080–1110); $\nu_{C=O}$ (1640–1680) are present. The band of stretching vibrations of the OH group in **7** appears at 3240 cm^{-1}.

Therefore, an efficient method of esterification of 1-germatranol with carboxylic acids allowing the preparation 1-acyloxygermatranes in high yields was developed.

EXPERIMENTAL

IR spectra were recorded on a Bruker Vertex-70 spectrometer in microlayer and in KBr. ^1H and ^{13}C NMR spectra were registered on a Bruker DPX-400 instrument (400.13 and 101.62 MHz respectively) in DMSO-d_6 (internal reference CH_3CN). Elemental analysis was performed on a Thermo Finigan FlashEA

Table 3. Data of ^{1}H, ^{13}C, and IR spectroscopy of 1-acetoxygermatranes **2**–**8**

Comp. no.	δ_H, ppm (J, Hz)	δ_C, ppm	ν, cm^{-1}
2	2.99 t (6H, NCH_2, $^3J_{HH}$ 5.7), 3.74 t (6H, OCH_2, $^3J_{HH}$ 5.7), 4.16 s (2H, CH_2Cl)	51.07 (NCH_2), 56.79 (OCH_2), 42.78 (CH_2Cl), 166.32 (C=O)	1728 v.s
3	2.99 t (6H, NCH_2, $^3J_{HH}$ 5.6), 3.75 t (6H, OCH_2, $^3J_{HH}$ 5.6), 6.45 d (1H, CH=C<u>H</u>), 7.38~7.65 m (5H, C_6H_4C<u>H</u>=CH)	51.12 (NCH_2), 56.67 (OCH_2), 121.79 (PhCH=<u>C</u>H), 127.92 (C^m), 128.85 (C^n), 129.77 (CH^o), 134.58 (C^{ipso}), 142.29 (Ph<u>C</u>H=CH), 165.86 (C=O)	1659 v.s 1622 w (CH=CH)
4	3.01 t (6H, NCH_2, $^3J_{HH}$ 5.6), 3.77 t (6H, OCH_2, $^3J_{HH}$ 5.6), 7.44 t (2H, CH^m, $^3J_{HH}$ 7.4), 7.55 t (1H, CH^n, $^3J_{HH}$ 7.2), 7.87 d (2H, CH^o, $^3J_{HH}$ 7.2)	51.16 (NCH_2), 56.76 (OCH_2), 128.28 (CH^m), 129.24 (CH^o), 131.89 (C^{ipso}), 132.04 (C^n), 167.39 (C=O)	1660 v.s
5	3.01 t (6H, NCH_2, $^3J_{HH}$ 5.6), 3.77 t (6H, OCH_2, $^3J_{HH}$ 5.6), 7.21~7.76 m (4H, C_6H_4)	51.12 (NCH_2), 56.75 (OCH_2), 116.52–116.74 (C^m), 121.61–121.70 (C^{ipso}), 124.07 (C^o), 131.73 (C^p), 133.57–133.65 (C^o), 159.50–162.04 (C^o), 163.09 (C=O)	1683 v.s
6	3.02 t (6H, NCH_2, $^3J_{HH}$ 5.5), 3.78 t (6H, OCH_2, $^3J_{HH}$ 5.6), 7.44 t (1H, CH^m, $^3J_{HH}$ 7.9), 7.77 d (1H, CH^n, $^3J_{HH}$ 7.7), 7.85 d (1H, CH^o, $^3J_{HH}$ 7.7), 7.95 s (1H, CH^2)	51.10 (NCH_2), 56.78 (OCH_2), 121.45 (C^{ipso}), 128.27 (C^o), 130.68 (C^m), 131.74 (C^o), 134.80 (C^p), 135.15 (C^m), 163.97 (C=O)	1687 v.s
7	3.00 t (6H, NCH_2, $^3J_{HH}$ 5.3), 3.80 t (6H, OCH_2, $^3J_{HH}$ 5.3), 9.57 s (OH), 6.90~7.30 m (4H, C_6H_4)	51.13 (NCH_2), 56.72 (OCH_2), 116.00 (C^p), 119.04 (C^o), 120.09 (C^m), 129.24 (C^o), 134.24 (C^{ipso}), 157.21 (C^m), 165.49 (C=O)	1668 s, 1682 v.s 3370 (OH)
8	3.01 t (6H, NCH_2, $^3J_{HH}$ 5.6), 3.77 t (6H, OCH_2, $^3J_{HH}$ 5.6), 1.33 t (3H, CH_3, $^3J_{HH}$ 6.9), 4.04 q (2H, OCH_2CH_3, $^3J_{HH}$ 6.9), 7.09~7.45 m (4H, C_6H_4)	14.56 (CH_3), 51.13 (NCH_2), 56.72 (OCH_2), 63.15 (OCH_2CH_3), 114.63 (C^o), 118.35 (C^o), 121.52 (C^m), 129.35 (C^n), 134.35 (C^{ipso}), 158.32 (COC_2H_5), 165.24 (C=O)	1683 v.s

1112 gas analyzer. Melting points were determined on a Micro-Hot-Stage PolyTherm A unit.

Solvents (diethyl ether, acetonitrile, methanol, isopentanol, *o*-xylene) were dried by the known procedures [16]. Germanium dioxide, chloroacetic, cinnamic, benzoic, 2-fluoro-, 3-bromo-, 3-hydroxy- and 3-ethoxybenzoic acid of analytical grade were used without additional purification. 1-Hydroxygermatrane hydrate **1** was synthesized from germanium dioxide and triethanolamine by the procedure described in [17].

1-(Chloroacetoxy)germatrane (2). The solution of 1.0 g (3.94 mmol) **1**, 0.372 g (3.94 mmol) of chloroacetic acid in 40 mL of acetonitrile were heated at reflux for 6 h, the solvent was removed at 80°C to the residual volume of 2–3 mL. The remained acetonitrile and the formed water were removed in a vacuum (2 mmHg). Colorless solid residue was kept in the same vacuum at 50°C for 1 h to obtain 1.203 g of colorless solid compound consisting of 83.4% of 1-(chloroacetoxy)germatrane **2**, 8.5% of **1** and 8.1% of chloroacetic acid (hereinafter the composition of the reaction residue is given in molar % estimated from the integral intensity of signals in the ^1H NMR spectra). The increased time of heating to 12 h led to the following composition of the reaction residue: 85.5% of **2**, 7.0% of **1** and 7.5% of chloroacetic acid. Crystallization from acetonitrile gave 0.950 g (77.2%) of **2**.

1-(Benzylideneacetato)germatrane (3). *a*. The solution of 1.0 g (3.940 mmol) of **1**, 0.584 g (3.94 mmol) of cinnamic acid in 40 mL of isopentanol was heated to reflux with the Dean-Stark trap for 6 h, the solvent was removed at 130°C to the residual volume ~5 mL, the concentrate was cooled to 25°C, 10 mL of dry diethyl ether was added and the mixture was left to stay overnight. The formed precipitate was filtered off, washed with dry diethyl ether (2 × 10 mL), and dried for 2 h at 25°C in a vacuum of 2 mmHg. 1.44 g of colorless product was obtained containing (from the data of ^1H NMR spectra in the mixture DMSO-d_6 :

CCl_4, 1 : 1) 50.6% of 1-(benzylideneacetato)germatrane **3**, 5.1% of 1-isoamyloxygermatrane **9**, 26.5% of **1**, 3.2% of bis(germatran-1-yl)oxane **11**, and 14.6% of cinnamic acid. The increased time of heating to 15 h resulted ine the reaction mixture of the following composition (from ^{1}H NMR spectra): 66.3% of **3**, 5.5% of **9**, 17% of **1**, 2.2% of **11**, and 9% of cinnamic acid.

b. The solution of 0.5 g (2.121 mmol) of **1**, 0.314 g (2.121 mmol) of cinnamic acid in 5 mL of methanol was heated to reflux for 3 h, the methanol and the formed water were removed in a vacuum (2 mmHg) to give 0.74 g of viscous mass consisting according to the ^{1}H NMR data of 6% of **3**, 4.1% of 1-methoxygermatrane **10**, 40.7% of **1**, 2.5% of **11**, and 46.7% of cinnamic acid. After additional keeping the residue in a vacuum of 2 mmHg at 50°C for 1 h the composition changed to **3 : 10 : 1 : 11** : cinnamic acid = 39.3 : 9.5 : 18.2 : 2.0 : 31.0.

c. The solution of 0.314 g (2.121 mmol) of cinnamic acid and 0.5 g (2.121 mmol) of **1** in 5 mL of the mixture MeOH–H_2O (9 : 1 v/v) was refluxed for 3 h. After removal of methanol and the formed water in a vacuum of 2 mmHg 0.8 g of colorless residue was obtained having the following composition: **3 : 10 : 1 : 11** : cinnamic acid = 3.5 : 4.8 : 41.6 : 0.9 : 49.2. After additional keeping this residue in a vacuum of 2 mmHg at 50°C for 1 h its composition changed to **3 : 10 : 1 : 11** : cinnamic acid = 17.8 : 0.6 : 40.7 : 1.1 : 39.7.

d. The solution of 1.0 g (3.940 mmol) of **1**, 0.584 g (3.940 mmol) of cinnamic acid in 40 mL of acetonitrile was refluxed for 6 h, the solvent was removed to the residual volume of 2–3 mL. The remained acetonitrile and the formed water were removed in a vacuum of 2 mmHg to the formation of colorless solid residue. After exposure of this residue to the same vacuum at 50°C for 1 h 1.450 g of the mixture was obtained containing 81.7% of **3**, 4.4% of **1**, 10.1% of cinnamic acid and 3.8% of **11**. Cinnamic acid was removed by treating the mixture with anhydrous diethyl ether and decantation. The crystallization of the dry residue from acetonitrile gave 1-(benzylideneacetato)germatrane **3** in 1.18 g (81.8%) yield as colorless needle crystals.

1-Benzoyloxygermatrane (4). *a*. After refluxing for 1 h of 1.221 g (0.01 mol) of benzoic acid and 2.538 g (0.01 mol) of **1** in 50 mL of isoamyl alcohol with azeotropic distillation of water and subsequent treatment of the reaction mixture as described above 2.78 g (82.0%) of 1-benzoyloxygermatrane **4** was obtained. mp 257–262°C. Literature: mp 257–260°C [12].

b. The solution of 1.0 g (3.940 mmol) of **1** and 0.481 g (3.940 mmol) of benzoic acid in 20 mL of methanol was refluxed for 7 h, methanol and the formed water were removed in a vacuum of 2 mmHg to obtain 1.17 g of colorless precipitate of the following composition: 18.7% of **3**, 40.5% of **1**, 1.6% of **11** and 39.2% of benzoic acid.

c. The mixture of 0.5 g (0.197 mmol) of **1** and 0.240 g (0.197 mmol) of benzoic acid in 5 mL of acetonitrile was refluxed for 1 h, the solvent and the formed water were removed in a vacuum of 2 mmHg. The colorless solid residue was kept in the same vacuum at 50°C for 1 h to obtain 1.203 g of colorless solid compound consisting of 88.6% of **4**, 6.2% of **1** and 5.2% of benzoic acid.

1-(2'-Fluorobenzoyloxy)germatrane (5). The solution of 1.0 g (3.940 mmol) of **1**, 0.552 g (3.940 mmol) of 2-fluorobenzoic acid in 40 mL of acetonitrile was refluxed. After 2 and 4 h the samples of 0.5 mL of the solution were taken for monitoring the reaction progress by ^{1}H NMR spectroscopy. After 2 h the mixture contained 10.5% of 1-(2'-fluorobenzoyloxy) germatrane **5**, 44.3% of **1**, and 45.2% of 2-fluorobenzoic acid; after 4 h 36.6% of **5**, 31.2% of **1**, and 32.2% of 2-fluorobenzoic acid. After 6 h acetonitrile was removed at 80°C to the beginning of formation of crystals, cooled, the formed crystalline precipitate was separated by decantation and kept at 2 mmHg at 50°C for 1 h. The yield of 1-(2'-fluorobenzoyloxy)germatrane **5** was 1.303 g (92.4%). After evaporation of the mother liquor to dryness and keeping in a vacuum of 2 mmHg at 50°C for 1 h additional 0.102 g (7.2%) of **5** with mp 223–226°C was obtained.

1-(3'-Bromobenzoyloxy)germatrane (6). The solution of 1.0 g (3.940 mmol) of **1**, 0.792 g (3.940 mmol) of 3-bromobenzoic acid in 40 mL of acetonitrile was refluxed for 6 h, the solvent was removed at 80°C to the residual volume 2–3 mL. The remained acetonitrile and the formed water were removed in a vacuum of 2 mmHg. Colorless solid residue was kept in the same vacuum at 50°C for 1h. It consisted of 93.3% of 1-(3'-bromobenzoyloxy)germatrane **6**, 3.1% of **1**, 0.7% of bis(germatran-1-yl)oxane **11**, and 2.8% of 3-bromobenzoic acid. Crystallization from acetonitrile gave 1.485 g (90.0%) of colorless crystals of **6**.

1-(3'-Hydroxybenzoyloxy)germatrane (7). *a*. The solution of 0.750 g (2.954 mmol) of **1**, 0.430 g (3.113 mmol) of 3-hydroxybenzoic acid in 120 mL of dry *o*-xylene was heated with the Dean-Stark trap at

142°C for 7 h, then a sample of 1 mL was taken, the solvent was removed, washed with dry diethyl ether, and dried in a vacuum of 2 mmHg for 1 h. 0.02 g of a solid residue was obtained consisting of 69.6% of 1-(3'-hydroxybenzoyloxy)germatrane **7**, 14.4% of **1**, and 16.1% of unreacted acid. The reaction mixture was refluxed for 10 h, the precipitate formed upon cooling was filtered off, washed with diethyl ether, and dried in a vacuum of 2 mmHg for 1 h. According to ^{1}H NMR spectrum (DMSO-d_6) the residue consisted of 98.3% of **7** and 1.7% of **1**. The crystallization from acetonitrile gave 0.980 g (93.5%) of **7** with mp 222–223°C.

b. The solution of 1.0 g (3.940 mmol) of **1**, 0.544 g (3.940 mmol) of 3-hydroxybenzoic acid in 40 mL of isoamyl alcohol was refluxed with the Dean-Stark trap. To monitor the reaction, 1 mL of the solution was taken off after 3 and 6 h of heating, the solvent was removed, the residue was washed with dry ether and dried in a vacuum of 2 mmHg for 1 h. From the data of ^{1}H NMR, after 3 h the residue contained 43.2% of **7**, 27.8% of **1**, and 29.0% of 3-hydroxybenzoic acid, and after 6 h, 80.5% of **7**, 9.4% of **1**, and 10.1% of 3-hydroxybenzoic acid. After 12 h of reflux 1.2 g of the residue was obtained containing 94.0% of **7**, 3.0% of **1** and 3.0% of 3-hydroxybenzoic acid. The reaction mixture was washed with dry acetonitrile (3 × 10 mL), kept in a vacuum of 2 mmHg for 1 h to obtain 1.120 g (79.9%) of fine-crystalline germatrane **7** with mp 221–222°C. Found, %: C 44.31, H 4.92, N 3.97, Ge 19.88. $C_{13}H_{17}NGeO_6$. Calculated, %: C 43.87, H 4.81, N 3.94, Ge 20.40.

1-(3'-Ethoxybenzoyloxy)germatrane (8). *a*. From 1.0 g (3.940 mmol) of **1**, 0.655 g (3.940 mmol) of *m*-ethoxybenzoic acid in 150 mL of *o*-xylene after reflux for 17 h was obtained 1.507 g of the product containing 29.8% of 1-(3'-ethoxybenzoyloxy)germatrane **8**, 36.5% of 1-germatranol **1**, and 33.6% of unreacted acid.

b. A mixture of 1.0 g (3.940 mmol) of **1**, 0.655 g (3.940 mmol) of *m*-ethoxybenzoic acid in 40 mL of isoamyl alcohol was refluxed with the Dean-Stark trap. The yield of 1-(3'-ethoxybenzoyloxy)germatrane **8** after 3 and 12 h of reflux was 47.0% and 79.3%, respectively.

c. A mixture of 1.0 g (3.940 mmol) of **1**, 0.655 g (3.940 mmol) of *m*-ethoxybenzoic acid in 40 mL of acetonitrile was refluxed for 7 h. Acetonitrile was removed at 80°C to the volume of 2–3 mL. The remained acetonitrile and the formed water were removed in a vacuum of 2 mmHg to obtain a viscous residue consisting of 79.5% of **8**, 9.8% of **1**, and 10.7% of *m*-ethoxybenzoic acid. After keeping in a vacuum of 2 mmHg at 50°C for 1 h 1.513 g of a paste-like mass was obtained, which solidified after 2 days. The composition was as follows: 86.2% of **8**, 6.3% of **1**, and 7.6% of *m*-ethoxybenzoic acid. Crystallization from chloroform gave 1.22 g (80.6%) of **8** containing 1.5% of **1**.

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